

(12) UK Patent Application (19) GB (11) 2 141 141 A

(43) Application published 12 Dec 1984

(21) Application No 8414863

(22) Date of filing 11 Jun 1984

(30) Priority data

(31) 501212

(32) 10 Jun 1983

(33) US

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(51) INT CL³

C25D 3/38

(52) Domestic classification

C7B 120 432 434 436 440 444 447 450 456 458

462 463 464 465 475 721 DL

U1S 2253 3035 C7B

(56) Documents cited

GB A 2097020=

GB 1526076

US 3770598

US 4336114

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US 3328273

GB A 2069536=

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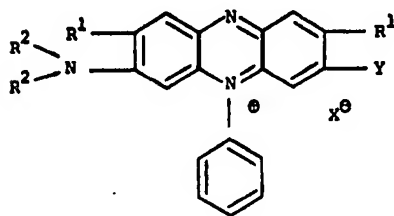
(58) Field of search

C7B

(54) Electrodepositing copper

(57) An aqueous acidic solution contains copper in an amount sufficient to electrodeposit copper on a substrate and a controlled combination of bath soluble and compatible organic brightening agents including:

- (1) one or more organic polyether compounds;
- (2) one or more organic sulphide compounds; and
- (3) at least one compound selected from each of:
 - (A) A 5-phenylphenazinium derivative having the formula:



(B) a substituted phthalocyanine, and

(C) an alkylated polyethyleneimine reaction product having a quaternary nitrogen.

The bath enables the deposition of a non-annealing engineering copper plate suitable for mechanical engraving. The plate may be on a rotogravure cylinder.

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SPECIFICATION

Process and bath for electrodepositing copper

- 5 The present invention broadly relates to the electrodeposition of copper deposits on conductive substrates, and more particularly is directed to the electroplating of rotogravure cylinders employed for printing providing an engineering copper plate which is eminently suitable for subsequent mechanical engraving. 5
- A variety of copper electrolyte compositions and processes have heretofore been employed for depositing a copper plate on the surfaces of rotogravure cylinders at a thickness sufficient to enable subsequent engraving thereof. Copper electrolytes of the type employed for depositing a bright decorative copper plate provide for good levelling and ductility of the copper deposit but are subject to the disadvantage that the copper deposit after deposition is self-annealing whereby the deposit becomes progressively softer following the plating step making the deposit unsatisfactory for mechanical engraving such as by employing a diamond stylus. Alternatively, copper electrolytes have been employed which do not self-anneal but such copper plates are characterized by their dull matt appearance with poor levelling necessitating mechanical finishing such as by polishing of the copper deposit to place it in condition for subsequent engraving. 10
- 20 The present invention provides for a process employing an aqueous acidic copper electrolyte which under controlled conditions is effective to deposit a substantially uniformly hard, non-annealing, bright, levelled and ductile engineering copper deposit which substantially eliminates or minimizes subsequent mechanical finishing operations of the copper deposit and wherein the copper deposit itself is of satisfactory hardness in spite of standing for prolonged time periods following the electrodeposition step to enable satisfactory engraving by various mechanical means. The process is further characterized as being of simple and economical control and operation for achieving consistent copper plates of the desired mechanical properties. 25
- The benefits and advantages of the present invention are based on the discovery of a process employing an aqueous acidic copper electrolyte of a controlled composition which under controlled operating parameters is operative for electrodepositing a highly levelled, ductile, bright and substantially uniformly hard engineering copper plate which is of a non-annealing character thereby retaining its hardness for prolonged time periods following the electrodeposition step enabling the plate to be engraved by mechanical engraving techniques and the like. 30
- The copper electrolyte comprises an aqueous acidic solution containing copper in an amount sufficient to electrodeposit copper on a substrate and a controlled combination of bath soluble and compatible organic brightening agents including: 35
- (1) one or more organic polyether compounds;
 - (2) one or more sulphide compounds, and
 - (3) at least one compound selected from each of:
- 40 (A) A compound corresponding to the structural formula A, 40

FORMULA A



- wherein R¹ and R² independently represent radicals selected from hydrogen, methyl and ethyl, X represents an anion selected from chloride, bromide, iodide, fluoride, sulphate, bisulphate and nitrate, Y represents H, -NH₂, -N(CH₃)₂ or -N=N-Z, and Z represents an aromatic radical selected from phenyl, naphthyl, and phenyl and naphthyl radicals substituted with amino, alkyl substituted amino, hydroxy and/or alkoxy substituent groups; 55
- (B) a substituted phthalocyanine compound corresponding to formula B, 60

60 FORMULA B

PcX_n

wherein:

- 65 Pc represents a phthalocyanine radical; 65

X represents $-\text{SO}_2\text{NR}_2$, $-\text{SO}_3\text{M}$ or $-\text{[CH}_2\text{SC(NR}_2\text{)]}_n\text{Y}$

R represents a hydrogen atom, an alkyl group containing 1 to 6 carbon atoms, an aryl group containing 6 carbon atoms, an aralkyl group containing 6 carbon atoms in the aryl portion 1 to 6 carbon atoms in the alkyl portion, or a heterocyclic group containing 2 to 5 carbon atoms and at least 1 nitrogen, oxygen, sulphur or phosphorus atom, each of the alkyl, aryl, aralkyl and heterocyclic groups, as defined above, optionally being substituted with 1 to 5 amino, hydroxy, sulphonic or phosphonic groups;

n is an integer of from 1 to 6

Y represents a halogen atom or an alkyl sulphate group containing 1 to 4 carbon atoms in the alkyl portion; and

M represents a hydrogen, lithium, sodium potassium or magnesium atom;

(C) an alkylated polyethyleneimine reaction product having a quaternary nitrogen atom.

The organic brightening agents in the aqueous acidic electrolyte may be present to provide a concentration of the polyether compound within a range of about 0.001 to about 5 grams per litre (g/l), the organic sulphide compound in a concentration of about 0.0005 to about 1 g/l, and a concentration of the brighteners comprising group (3) in admixture of about three or more present in an amount of at least about 25 milligrams (mg/l) with concentrations up to about 0.5 g/l being usable.

In accordance with the process aspects of the present invention, the aqueous acidic copper electrolyte may be employed at a temperature of about 60° to about 100°F (16° to 38°C) and the deposition of copper on a conductive substrate is performed at a cathode current density of at least about 60 amperes per square foot (ASF) (6.6 amperes per square decimetre (ASD)) up to as high as about 300 ASF (33 ASD) or higher to provide an engineering copper deposit of at least about 0.001 inch (26 microns) thick. A conforming anode or plurality of anodes is preferably employed to avoid any low current density areas less than about 60 ASF (6.6 ASD) and further to assure a substantially uniform thickness of copper deposit on the substrate.

Additional benefits and advantages of the present invention will become apparent upon a reading of the description of the preferred embodiments taken in conjunction with the accompanying examples.

In accordance with the practice of the process of the present invention, an aqueous acidic electrolyte is provided which may be of the sulphate type typically containing about 180 to about 250 g/l of copper sulphate and about 30 to about 80 g/l of sulphuric acid. Alternatively, fluoroborate baths can be prepared typically containing from about 200 to about 600 g/l of copper fluoroborate and up to about 60 g/l of fluoboric acid. It is also contemplated that copper nitrate salts or copper sulphamate salts can be employed in approximately equivalent proportions for copper sulphate and the electrolyte can be acidified employing equivalent amounts of phosphoric acid, nitric acid, sulphamic acid or sulphuric acid. In accordance with the preferred practice of the present invention, sulphate-type copper baths are employed.

The aqueous electrolyte may further incorporate halide ions such as chloride and/or bromide ions in an amount up to about 0.2 g/l. Concentration of halide ions in excess of about 0.2 g/l have been found undesirable in some instances due to a loss in the ductility of the copper deposit.

The unique non-annealing characteristics of the copper deposits in further combination with the desirable physical characteristics thereof are achieved by employing a specific combination of organic brighteners of the types as hereinbefore set forth. The preferred organic polyether compounds are bath soluble and compatible polyethers containing at least 4 ether oxygen atoms and having an average molecular weight ranging from about 180 up to 1,000,000. Particularly satisfactory results are obtained with polypropylene and polyethylene glycols including mixtures of the foregoing of an average molecular weight of about 600 to about 6,000, alkoxylated aromatic alcohols having a molecular weight ranging from about 300 to 2500 and alkoxylated amines having a molecular weight of about 1000 to about 50,000. Exemplary of such preferred polyether brightening compounds which can satisfactorily be employed are polyethylene glycols of an average molecular weight of from about 400 to about 1,000,000; ethoxylated naphthols containing 5 to 45 mols ethylene oxide groups; propoxylated naphthols containing 5 to 15 mols of propylene oxide groups; ethoxylated nonyl phenol containing 5 to 30 mols ethylene oxide groups; propylene glycols of an average molecular weight of about 350 to about 1,000; block polymers of polyoxyethylene and polyoxypropylene glycols of an average molecular weight of about 350 to 250,000; ethoxylated phenols containing 5 to 100 mols of ethylene oxide groups; propoxylated phenols containing 5 to 15 mols of propylene oxide groups, and ethylene diamine block polymers having a molecular weight of about 1600 to about 30,000. Additional polyether compounds suitable for use in the practice of the present process are those disclosed in United States Patent No. 4,272,335 the teachings of which are incorporated herein by reference.

The polyether brightening compounds are employed in a range of about 0.001 up to about 5 g/l with the lower concentrations generally being used with the higher molecular weight

polyethers.

The organic sulphide brightening compound (2) which can be satisfactorily employed in the practice of the present process includes the various organic sulphide sulphonc compounds as described in United States Patent No. 3,267,010 (particularly Table I thereof), the teachings of which are incorporated herein by reference; organic sulphur compounds as disclosed in United States Patent No. 4,181,582 (particularly Table III thereof), the substance of which is incorporated herein by reference; and the organic polysulphide compounds as disclosed in United States Patent No. 3,328,273 (particularly Table I thereof), the substance of which is also incorporated herein by reference. The organic sulphide compounds containing sulphonc or phosphonic groups may also contain various substituent groups, such as methyl, chloro, bromo, methoxy, ethoxy, carboxy or hydroxy, on the molecules, especially on the aromatic and heterocyclic sulphide-sulphonc or phosphonic acids. Such compounds may be used as the free acids, the alkali metal salts, organic amine salts, or the like.

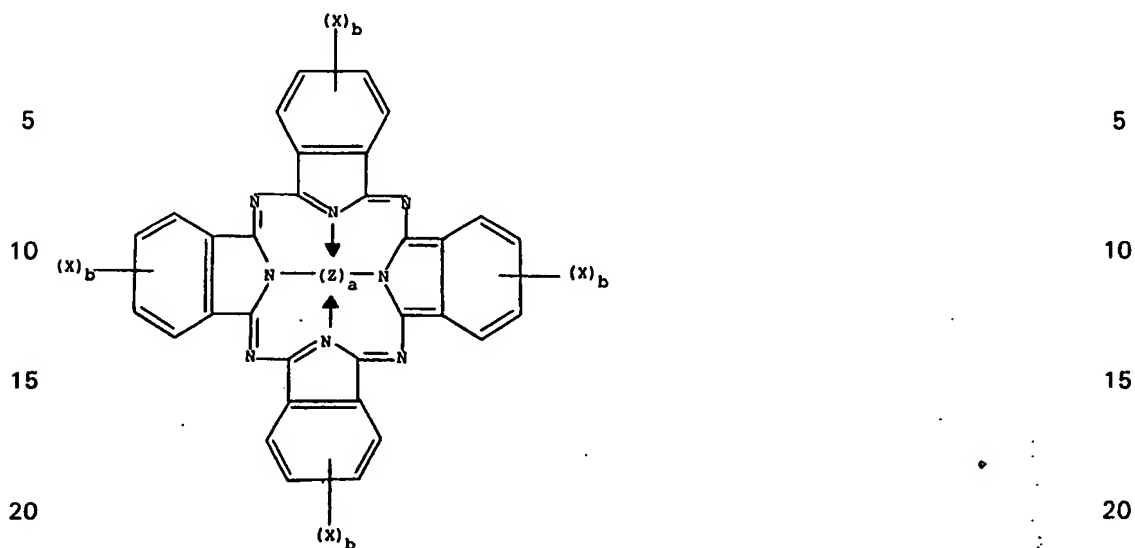
Other suitable organic divalent sulphur compounds which can be satisfactorily used include $\text{HO}_3\text{P}-(\text{CH}_2)_3-\text{S}-\text{S}-(\text{CH}_2)_3-\text{PO}_3\text{H}$, as well as mercaptans, thio-carbamates, thiolcarbamates, thioxanthates, and thiocarbonates which contain at least one sulphonc or phosphonic group.

A particularly preferred group of organic divalent sulphur compounds as described in U.S. Patent No. 3,328,273 are the organic polysulphide compounds of the formula $\text{XR}_1-(\text{S})_n\text{R}_2\text{SO}_3\text{H}$ or $\text{XR}_1-(\text{S})_n\text{R}_2\text{PO}_3\text{H}$ wherein R_1 and R_2 are the same or different alkylene group containing from about 1 to 6 carbon atoms, X is hydrogen, SO_3H or PO_3H and n is a number from about 2 to 5. These organic divalent sulphur compounds are aliphatic polysulphides wherein at least two divalent sulphur atoms are vicinal and wherein the molecule has one or two terminal sulphonc or phosphonic acid groups. The alkylene portion of the molecule may be substituted with groups such as methyl, ethyl, chloro, bromo, ethoxy, hydroxy, and the like. These compounds may be added as the free acids or as the alkali metal or amine salts.

The organic sulphide brightening compound or mixture of compounds are present in the electrolyte within a range of about 0.0005 to about 1 g/l.

In addition to the brightening agents (1) polyether compounds and (2) sulphide compounds, the electrolyte further contains as an essential brightening agent at least three brightener compounds (3) comprising at least one compound corresponding to each of formulae (A), (B), and (C). Brightening compound (A) corresponding to Formula (A) as hereinabove set forth is a 5-phenylphenazinium derivative and may typically comprise one or more of those as set forth in United States Patent No. 2,882,209, and specifically Table II thereof, the substance of which is incorporated herein by reference. Such typical brighteners include Diethyl safranine azo dimethyl aniline—Janus Green B, Diethyl safranine azo phenol—Janus Black, Safranine azo naphthol—Janus Blue, Janus Gray (Color Index 137, Society of Dyers & Colourists, by F. M. Rowe, 1924), Dimethyl safranine azo dimethyl aniline, Phenosafranine, Fuchsia, Amethyst Violet, and the like. Brightening compounds corresponding to Formula (A) can be employed within a range up to about 0.5 g/l with concentrations of about 25 to about 50 mg/l being preferred.

The brightening agent corresponding to Formula (B) comprises a substituted phthalocyanine radical which may be metal-free or which may contain a stable divalent or trivalent metal bound by coordination of the isoindole nitrogen atoms of the molecule, which metal is selected from cobalt, nickel, chromium, iron and copper. Copper is the more typical and preferred metal. More than one such compound may be present. Such phthalocyanine compounds suitable for use in the preferred practice of the present process are those having a bath solubility of at least about 0.1 mg/l and are employed in concentrations up to about 0.5 g/l with concentrations of about 25 to about 50 mg/l being preferred. Suitable phthalocyanine compounds correspond to the structural formula:



wherein:

X is as has been previously defined;

30 Z represents a nickel, cobalt, chromium, iron or copper atom;

a is 0 or 1; and

b is independently 0, 1 or 2, provided however that the total number of X substituent is from 1 to 6.

35 Substituents phthalocyanine compounds suitable for use in the practice of the present invention further include those as described in United States Patent No. 4,272,335, the teachings of which are incorporated herein by reference. A particularly preferred phthalocyanine compound comprises Alcian Blue.

The organic brightening compound (C) comprises a reaction product of polyethyleneimine and an organic compound which will alkylate the nitrogen of the polyethyleneimine to product a 40 quaternary nitrogen. Compounds of the foregoing type satisfactory for use in the practice of the present process are disclosed in United States Patent No. 3,770,598, the teachings of which are incorporated herein by reference. The alkylating agent may be an aliphatic or aromatic compound, either of which may be either saturated or unsaturated. Compounds which have proved to be of particular value are organic compounds which contain active halogens, such as 45 the alkyl halides, the alkyl, alkenyl and alkynyl halides, acid halides, acyl halides, and the like. Additionally, compounds such as the alkyl sulphates, alkyl sultones, aldehydes, ketones, isocyanates, thioisocyanates, epoxides, acylamides, acids, anhydrides, ureas, cyanamides, guanidines, and the like, may also be used. It is to be appreciated that in some instances organic compounds may be used in which the reacting group is attached directly to an aromatic 50 nucleus, rather than on an alkyl chain. Exemplary of such materials is 2,4-dinitrochlorobenzene, which will react with either the primary or secondary nitrogen of the polyethyleneimine and/or will quaternize the tertiary nitrogen. Accordingly, in referring to the "alkylation" of the nitrogen in the polyethyleneimine, it is intended to include those cases in which the nitrogen is attached directly to an aryl or aromatic nucleus, as well as those in which it is attached to an aliphatic 55 group. Specific compounds which have been found to give particularly good results are benzyl chloride, allyl bromide, dimethyl sulphate and propane sultone. These compounds, however, are merely exemplary of the organic compounds which will alkylate the nitrogen of the polyethyleneimine. Preferably the alkylating agent is an aromatic halide.

When the alkylating agent reacts with the primary or secondary amine, it will be altered to the 60 secondary or tertiary amine, respectively. This is accomplished by adding more alkylating agent as is desired. Where the alkylation takes place at the primary and/or secondary nitrogen, there will be a splitting off of the alkylating or leaving groups on the organic compound, e.g., halogen, sulphate, or the like. In the case of the tertiary nitrogen, however, a quaternization takes place, forming the quaternary salt.

65 It is preferred that as many nitrogen atoms as possible in the polyethyleneimine brightener

should be quaternized, although as little as 5 percent of the nitrogen atoms being quaternary still gives desirable results, with 10 percent being more preferred and even more preferably 20 percent.

The polyethyleneimine which is used in forming the brightening agent additive may have a wide range of molecular weights. Typically, the molecular weight of the polyethyleneimine may be within the range of about 300 to several millions. In many instances, however, molecular weights within the range of about 300 to 1,000,000 are preferred. The organic brightening compound (C) is employed in amounts up to about 0.5 g/l with concentrations of about 35 to about 100 mg/l being preferred.

The organic brightening agents (A), (B) and (C) are employed in combination of at least three in an amount of at least about 25 mg/l with concentrations up to about 0.5 g/l being satisfactory while amounts of about 30 to about 90 mg/l being preferred.

In accordance with the practice of the process of the present invention, an electrolyte of the foregoing composition is employed in which an electrically conductive substrate is immersed and is cathodically charged for a period of time to deposit the desired thickness of copper thereon. During the electroplating operation, the preferred temperature of the bath is within a range of about 60° up to about 100°F (16° to 38°C) with temperatures of from about 70° up to about 90°F (21° to 32°C) being typical and preferred. Temperatures above about 100°F (38°C) are undesirable in many instances due to the tendency to form copper deposits which are of reduced ductility. The electrodeposition of the copper plate is performed at a current density of at least about 60 ASF (6.6 ASD) to current densities as high as about 300 ASF (33 ASD) and even higher in specialized instances. Preferably, the cathode current density is controlled within a range of about 100 to about 200 ASF (11 to 22 ASD). In order to achieve a substantially uniform thickness of copper plate on the substrate, it is preferred that an anode arrangement is employed which provides for a substantially uniform current density on the cathode over substantially the entire surface thereof. For this purpose, in accordance with conventional practice in the electroplating of rotogravure cylinders, a conforming anode, or in the alternative, a plurality of anodes disposed at spaced intervals is employed so as to achieve a substantially uniform cathode current density.

The unique copper plate deposited in accordance with the practice of the present invention which is bright, levelled, ductile, substantially pure copper is eminently adapted for a variety of engineering applications such as for electroforming moulds, manufacture of audio and video discs, for rotogravure cylinders and the like. The copper plate is further characterized as being of relatively uniform hardness, usually above 200 Diamond Pyramid Hardness Number at a 100 gram load and further characterized by a highly uniform, homogeneous, equiaxed crystalline structure of a grain size less than about 1 micron. The engineering copper deposit produced by the present process is distinguishable from conventional decorative copper deposits because of the thickness which is at least about 0.001 inch to as high as 0.050 inch and even thicker as well as in the unique nonannealing characteristics of the engineering copper plate. The process of the present invention furthermore may not be so applicable for producing so-called decorative copper deposits due to the formation of dark striations in all low current density areas having average cathode current densities below 60 ASF (6.6 ASD) which renders such decorative deposit unacceptable.

In order to further illustrate the process of the present invention, the following typical examples are provided. It will be appreciated that the examples are provided for illustrative purposes and are not intended to be limiting of the scope of the present invention as herein described and as set forth in the subjoined claims.

EXAMPLES 1A and 1B

An aqueous acidic copper electrolyte is prepared containing about 195 g/l of copper sulphate pentahydrate, 75 g/l of sulphuric acid, about 20 (Example 1A) or about 100 mg/l (Example 1B) chloride ions and a combination of organic brightening agents comprising brighteners (1) polypropylene oxide (mol wt. 750) present in an amount of about 120 mg/l, (2) Bis (3-sulphopropyl) disulphide disodium salt) present in an amount of about 21 mg/l, brightener (3) corresponding to Formula (a) comprising Janus Green B present in an amount of about 15 mg/l, brightener (3) corresponding to Formula (B) comprising Methic Turquoise present in an amount of about 15 mg/l and brightener (3) (C) comprising polyethyleneimine quaternized with benzyl chloride present in an amount of about 12 mg/l.

In each case the bath is controlled at a temperature of about 80°F (27°C) and a rotogravure cylinder is immersed in the bath surrounded by conforming copper anodes while rotated at 100 rpm and electric current is passed between the anodes and cathodically charged work piece to provide a cathode current density of about 150 ASF (16.5 ASD). The resultant copper deposit is observed to be fully bright with good levelling, good ductility and of a substantially uniform hardness above 200 Diamond Pyramid Hardness Number at a 100 gram load (DPH). The copper deposit is substantially non-annealing as evidenced by no significant reduction in

hardness after standing for a period of 48 hours following the electrodeposition of the copper plating.

EXAMPLES 2A and 2B

- 5 An aqueous acidic copper electrolyte is prepared containing about 195 g/l of copper sulphate pentahydrate, 75 g/l of sulphuric acid, about 20 (Example 2A) or about 100 mg/l (Example 2B) chloride ions and a combination of organic brightening agents comprising brighteners (1) polyethylene oxide (mol wt. 3350) present in an amount of about 60 mg/l, (2) Bis (3-sulphopropyl disulphide disodium salt) present in an amount of about 30 mg/l, and brightener (3) corresponding to Formula (A) comprising Janus Green B present in an amount of about 10 mg/l, Methic Turquoise corresponding to formula B present in an amount of 10 mg/l and 10 mg/l of brightener (3) (C) comprising polyethyleneimine quaternized with benzyl chloride.

In each case the bath is controlled at a temperature of about 75°F (24°C) and a rotogravure cylinder is immersed in the bath surrounded by conforming copper anodes while rotated at 300 rpm and electric current is passed between the anodes and cathodically charged work piece provide an average cathode current density of about 100 ASF (11 ASD). The resultant copper deposit is observed to be fully bright, levelled and ductile with a hardness above about 200 DPH at 100 gram load. The resultant copper deposit is substantially nonannealing.

20 EXAMPLES 3A and 3B

- An aqueous acidic copper electrolyte is prepared containing about 195 g/l of copper sulphate pentahydrate, 75 g/l of sulphuric acid, about 20 (Example 3A) or about 100 mg/l (Example 3B) chloride ions and a combination of organic brightening agents comprising brighteners (1) polypropylene oxide (mol wt. 750) present in an amount of about 120 mg/l, (2) Bis (3-sulphopropyl disulphide disodium salt) present in an amount of about 30 mg/l, and brightener (3) corresponding to Formula (A) comprising Janus Green B present in an amount of about 8 mg/l, brightener (3) corresponding to Formula (B) comprising Methic Turquoise present in an amount of about 22 mg/l and brightener (3) corresponding to Formula (C) comprising poethyleneimine quaternized with benzylchloride present in an amount of about 3 mg/l.

30 In each case the bath is controlled at a temperature of about 70°F (21°C) and a rotogravure cylinder is immersed in the bath surrounded by conforming copper anodes while rotated at 180 rpm and electric current is passed between the anodes and cathodically charged work piece to provide an average cathode current density of about 150 ASF (16.5 ASD). The resultant copper deposit is observed to be fully bright, levelled and ductile with a hardness above 200 DPH at a 35 100 gram load. The copper deposit is substantially non-annealing.

While it will be apparent that the preferred embodiments of the invention disclosed are well calculated to fulfil the objects above stated, it will be appreciated that the invention is susceptible to modification, variation and change without departing from the proper scope or fair meaning of the subjoined claims.

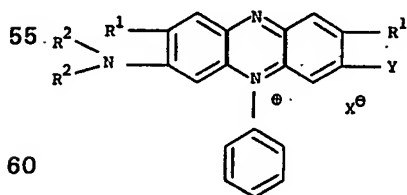
40 CLAIMS

1. A process for electrodepositing a highly levelled, ductile, bright, substantially uniformly hard nonannealing engineering copper plate on a conductive substrate comprising the steps of immersing a conductive substrate in an aqueous acidic solution containing copper in an amount 45 sufficient to electrodeposit copper on a substrate and a controlled combination of bath soluble and compatible organic brightening agents including:

- (1) one or more organic polyether compounds;
- (2) one or more organic sulphide compounds; and
- (3) at least one compound selected from each of:

- 50 (A) A compound corresponding to the structural formula A,

FORMULA A



wherein R¹ and R² independently represent radicals selected from hydrogen, methyl and ethyl radicals, X represents an anion selected from chloride, bromide, iodide, fluoride, sulphate, 65 bisulphate and nitrate, Y represents H, -NH₂, -N(CH₃)₂ or -N=N-Z, and Z represents an

aromatic radical selected from phenyl, naphthyl, and phenyl and naphthyl radicals substituted with amino, alkyl substituted amino, hydroxy and/or alkoxy substituent groups;

(B) a substituted phthalocyanine compound corresponding to formula B,

5 FORMULA B

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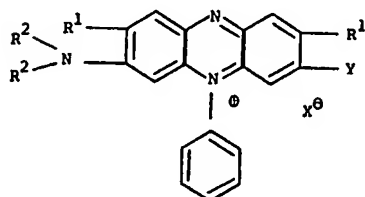
PcX_n

wherein:

- 10 Pc represents a phthalocyanine radical; 10
- X represents $-SO_2NR_2$, $-SO_3M$ or $-[CH_2SC(NR_2)_2]^+Y^-$;
- R represents a hydrogen atom an alkyl group containing 1 to 6 carbon atoms, an aryl group containing 6 carbon atoms, an aralkyl group containing 6 carbon atoms in the aryl portion and 1 to 6 carbon atoms in the alkyl portion, or a heterocyclic group containing 2 to 5 carbon atoms and at least 1 nitrogen, oxygen, sulphur or phosphorus atom, each of the alkyl, aryl, aralkyl and heterocyclic groups, as defined above, optionally being substituted with 1 to 5 amino, hydroxy, sulphonic or phosphonic groups; 15
- n is an integer of from 1 to 6;
- Y represents halogen or alkyl sulphate containing 1 to 4 carbon atoms in the alkyl portion 20
- and;
- M represents a hydrogen, lithium, sodium, potassium or magnesium atom; 20
- (C) an alkylated polyethyleneimine reaction product having a quaternary nitrogen; and passing electric current through the solution at an average cathode current density of at least about 60 ASF (6.6 ASD) to electrodeposit an engineering copper plate on the substrate to a thickness of at least about 0.001 inch (25 microns). 25
2. A process as claimed in Claim 1, in which brightening agent (1) is present in an amount of from 0.001 to 5 g/l.
3. A process as claimed in Claim 1 or 2, in which brightening agent (2) is present in an amount of from 0.0005 to 1 g/l.
- 30 4. A process as claimed in Claim 1, 2 or 3, in which the brightening agents (3) are present in a combined amount of at least 25 mg/l up to 0.5 g/l. 30
5. A process as claimed in any one of Claims 1 to 4, in which the brightening agents (3) are present in a combined amount of from 30 to 90 mg/l.
6. A process as claimed in any one of Claims 1 to 5, wherein the temperature of the aqueous acidic solution is kept during the step of electrodepositing the copper plate within a range of from 60° to 100°F (16° to 38°C). 35
7. A process as claimed in any one of Claims 1 to 6, wherein the temperature of the aqueous acidic solution is kept during the step of electrodepositing the copper plate within a range of from 70° to 90°F (21° to 32°C).
- 40 8. A process as claimed in any one of Claims 1 to 7, in which the step of electrodepositing a copper plate on the substrate is performed at an average cathode current density up to 300 ASF (33 ASD). 40
9. A process as claimed in any one of Claims 1 to 8, in which the step of electrodepositing a copper plate on the substrate is performed at an average cathode current density of from 100 to 200 ASF (22 ASD). 45
10. A process as claimed in any one of Claims 1 to 9 in which the aqueous acidic solution further contains halide ions up to 0.2 g/l.
11. A process as claimed in any one of Claims 1 to 10, wherein an anode immersed in the solution is arranged relative to the substrate to provide a substantially uniform cathode current density within a range of from 60 to 300 ASF (6.6 to 33 ASD). 50
12. A process as claimed in any one of Claims 1 to 10, in which the conductive substrate comprises a rotogravure cylinder and wherein the cylinder is rotated during the step of electrodepositing the copper plate thereon to provide a substantially uniform thickness of copper plate thereon.
- 55 13. A bright, levelled, ductile, substantially nonannealing, substantially pure engineering copper plate of substantially uniform hardness produced in accordance with a process as claimed in any one of Claims 1 to 12. 55
14. An engineering bright, levelled, ductile, substantially nonannealing, substantially pure copper deposit comprising a matrix of highly uniform, homogeneous, equiaxed crystalline structure of an average grain size less than about 1 micron, the crystalline structure being stable without the tendency of recrystallize after electrodeposition. 60
15. An aqueous acidic solution containing copper in an amount sufficient to electrodeposit copper on a substrate and a controlled combination of bath soluble and compatible organic brightening agents including: 65
- (1) one or more organic polyether compounds; 65

- (2) one or more organic sulphide compounds; and
 (3) at least one compound selected from each of:
 (A) A compound corresponding to the structural formula A,

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- 15 wherein R¹ and R² independently represent radicals selected from hydrogen, methyl and ethyl radicals, X represents an anion selected from the chloride, bromide, iodide, fluoride, sulphate, bisulphate and nitrate, Y represents H, -NH₂, -N(CH₃)₂ or -N=N-Z, and Z represents an aromatic radical selected from phenyl, naphthyl, and phenyl and naphthyl radicals substituted with amino, alkyl substituted amino, hydroxy and/or alkoxy substituent groups;
 20 (B) a substituted phthalocyanine compound corresponding to formula B,

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FORMULA B

PcX_n

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wherein:

Pc represents a phthalocyanine radical;

X represents -SO₂NR₂, -SO₃M or -[CH₂SC(NR₂)₂][⊕]Y[⊖];

- 30 R represents a hydrogen atom, an alkyl group containing 1 to 6 carbon atoms, an aryl group containing 6 carbon atoms, an aralkyl group containing 6 carbon atoms in the aryl portion and 1 to 6 carbon atoms in the alkyl portion, or a heterocyclic group containing 2 to 5 carbon atoms and at least 1 nitrogen, oxygen, sulphur or phosphorus atom, each of the alkyl, aryl, aralkyl and heterocyclic groups, as defined above, containing 1 to 5 amino, hydroxy, sulphonic or phosphonic groups;

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- 35 n is an integer of from 1 to 6;

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Y represents halogen or alkyl sulphate containing 1 to 4 carbon atoms in the alkyl portion; and

M represents a hydrogen, lithium, sodium, potassium or magnesium atom;

(C) an alkylated polyethyleneimine reaction product having a quaternary nitrogen.

- 40 16. A solution as claimed in Claim 15, in which brightening agent (1) is present in an amount of from 0.001 to 5 g/l.

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17. A solution as claimed in Claim 15 or 16 in which brightening agent (2) is present in an amount of from 0.0005 to 1 g/l.

- 45 18. A solution as claimed in Claim 15, 16 or 17 in which the brightening agents (3) are present in a combined amount of at least 25 mg/l up to 0.5 g/l.

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19. A solution as claimed in any one of Claims 15 to 18 in which the brightening agents (3) are present in a combined amount of from 30 to 90 mg/l.

20. A solution as claimed in any one of Claims 15 to 19, in which the aqueous acidic solution further contains halide ions up to 0.2 g/l.

- 50 21. A process substantially as hereinbefore described with reference to any one of the Examples.

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22. A solution substantially as hereinbefore described with reference to any one of the Examples.